

OXIDATION OF ETCHED SILICON IN AIR AT ROOM TEMPERATURE; MEASUREMENTS WITH ULTRASOFT X-RAY PHOTOELECTRON SPECTROSCOPY (ESCA) AND NEUTRON ACTIVATION ANALYSIS

G. MENDE

Zentralinstitut für Kernforschung der Akademie der Wissenschaften der DDR, Rossendorf, Bereich 2, Postfach 19, DDR-8051 Dresden, German Dem. Rep.

and

J. FINSTER, D. FLAMM and D. SCHULZE

Karl-Marx-Universität, Sektion Chemie, Linnéstrasse 2, DDR-7010 Leipzig, German Dem. Rep.

Received 29 November 1982

The oxide growth rate for p-type Si(100) crystals after HF etching in air at room temperature was measured for exposures between 3 min and $\approx 10^3$ min after etching. The oxide thicknesses were determined with traditional Al K α excited XPS and two nontraditional methods – especially suited for very thin layers: Zr M ζ excited XPS and neutron activation analysis (NAA). The oxide thicknesses (mainly SiO $_x$ with $x < 2$) lie between 0.1 and 0.55 nm with a logarithmic growth rate of ≈ 0.2 nm/decade.

1. Introduction

During electronic device fabrication silicon often comes in contact with HF. The oxidation of HF etched silicon single crystals in air at room temperature is of practical importance in semiconductor processing, e.g. for electronic devices with ultrathin silicon dioxide films ($d = 4\text{--}10$ nm) and for production of electrical contacts on silicon.

Archer [1] and Lukeš [2] measured by ellipsometry the oxide growth on silicon after etching with mixtures of nitric acid, hydrofluoric acid and acetic acid. Raider, Flitsch and Palmer [3] investigated the oxidation of silicon after etching with HF solution, comparing ellipsometric with ESCA measurements, and starting with 1 h air exposure.

They found an overestimate of the oxide thicknesses by ellipsometry, which was explained by the influence of impurity films on the ellipsometric measurement. However, the thickness determination by means of ESCA is not free

from imperfections either. One of the drawbacks of the electron spectroscopic methods is that the decisive parameter for thickness determination, the mean electron escape depth (depth from which 63% of the total intensity originates), is only known with a rather low accuracy.

Therefore we tried to investigate the oxidation of HF etched silicon in air at room temperature by ESCA in comparison with another measurement which is independent of thickness – the neutron activation analysis (NAA) of the Si content of the oxide layers [4]. Moreover, we used – as an extension of ESCA measurements to lower air exposure times (< 1 h) – the Zr $M\zeta$ radiation in combination with the Al $K\alpha$ excitation.

2. Experimental

2.1. ESCA

Polished and cleaned $\langle 100 \rangle$ oriented samples of p-type silicon ($10 \Omega \text{ cm}$) were etched in 1N HF solution. Then the samples were dipped into saturated boric acid solution in water and rinsed in deionized water and in absolute alcohol. After drying, the samples were exposed for a definite time to air at room temperature and then introduced into the vacuum (minimum air contact 5 min) of the ESCA spectrometer “Vacuum Generators ESCA 3”, equipped with an Al/Zr twin anode [5]. Spectra were taken successively with Al $K\alpha$ (1486.6 eV) and Zr $M\zeta$ (151.4 eV) excitation in a vacuum of $\approx 10^{-7}$ Pa.

2.2. NAA

Polished and cleaned $\langle 100 \rangle$ oriented samples of p-type silicon ($10 \Omega \text{ cm}$) were irradiated for 1 h in the Rossendorf research reactor with a neutron flux of about $4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ to transmute the ^{30}Si content into the radioactive isotope ^{31}Si by the thermal neutron capture reaction $^{30}\text{Si}(n, \gamma)^{31}\text{Si}$. After cleaning and an annealing treatment in a nitrogen atmosphere at 800°C for half an hour the samples were cleaned ($\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$) and etched in 1N HF. Then the samples were dipped into saturated boric acid solution in water and rinsed in deionized water and absolute alcohol. After drying the samples were mounted in a Teflon etch beaker, where a portion of the surface was masked to determine a definite area for oxidation and etching. After exposure to air for a definite time the samples were etched several times for 1 min with HF solution, interrupted by rinsing in the above mentioned way (boric acid, etc.). The radioactivity of the solution of each 1 min etching was counted in a Geiger–Müller counter [4].

3. Thickness determination

3.1. ESCA

The evaluation of the ESCA data was done essentially in the same way as in ref. [6]. The Si 2p line shows additional intensity on the high binding energy (BE) side, compared with the spectrum of a clean Si surface. It develops to a double peak structure with increasing exposure. Fig. 1 presents this developing structure for Zr $M\zeta$ excitation; for Al $K\alpha$ excitation the lines are narrower and the oxide intensity is much lower because of the higher escape depth.

From these Si 2p spectra the line of the elemental silicon (clean substrate line) was subtracted as a symmetrical line with a FWHM of 1.35 eV (Al $K\alpha$) or 1.6 eV (Zr $M\zeta$) on an average at the position of the first maximum (normally 99.4 eV BE, see fig. 1a). The remaining intensity was taken as a general oxide intensity, not differentiating into SiO_2 and SiO_x ($x < 2$) parts.

From the BE shift of the second maximum (< 3.8 eV, see ref. [6]), we can conclude, that in almost all cases the oxide layer consists essentially of SiO_x .

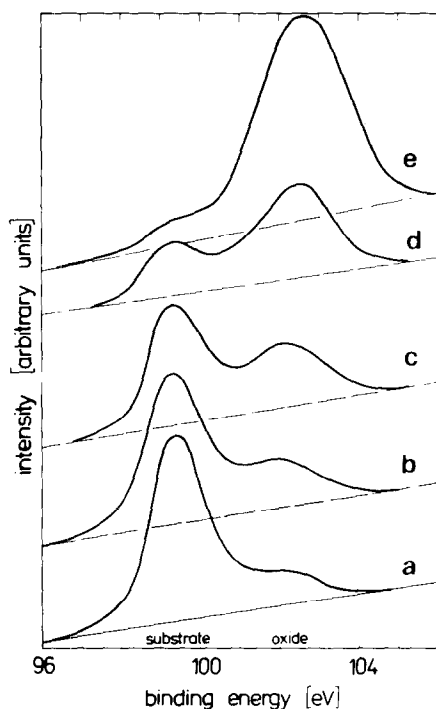


Fig. 1. Zr $M\zeta$ excited Si 2p spectra with increasing exposure to air: (a) 5 min, (b) 10 min, (c) 55 min, (d) 490 min, (e) before etching.

Therefore we chose for the evaluation a model with a single layer, approximated with a SiO stoichiometry ($x = 1$). From the intensity ration Si 2p(oxide)/Si 2p(element) we calculated the thickness d_{SiO} with the well-known formulas (see, e.g., ref. [6]). As intensity ratio $I_{\infty}(\text{SiO})/I_{\infty}(\text{Si})$ we used 0.61, the escape angle α was 30° , and the escape depths were taken as in ref. [6] for Al K α excitation ($\lambda_{\text{Si}} = 2.5$ nm, $\lambda_{\text{SiO}} = 2.6$ nm) and from ref. [7] for Zr M ζ excitation ($\lambda_{\text{Si}} \approx \lambda_{\text{SiO}} = 0.65$ nm).

3.2. NAA

The measured radioactivity of the etch solutions was transferred into an absolute Si content by comparison with the radioactivity of a standard solution. This standard solution was prepared by dissolving a neutron irradiated p-type Si crystal of known weight in HF/HNO₃ and diluting and aliquoting the solution [8]. The dissolution rate of elemental Si in HF, determined in the above mentioned way without exposure of Si to air (see also refs. [8,9]) was subtracted. From the Si amount per given wafer area, (g Si)/ F , determined in this manner, the oxide (SiO) layer thickness was derived according to the following equation:

$$d_{\text{SiO}} = \frac{g \text{ Si}}{F} \frac{M_{\text{SiO}}}{A_{\text{Si}}} \frac{1}{\rho_{\text{SiO}}},$$

where M = molecular mass, A = atomic mass and ρ_{SiO} (density) ≈ 2.3 g/cm³ [6].

4. Results and discussion

The intensity ratios Si 2p(oxide)/Si 2p(element) and the thicknesses determined in the ESCA measurements with Al K α and Zr M ζ excitations are given in table 1. The error of the thicknesses is $\leq \pm 20\%$, stemming to about equal contributions from the error of the intensity ratios and from the uncertainties of the λ -values. Although, with a fixed set of λ -values, the relative thicknesses within a certain series of measurements are more exact, for the determination of absolute values and for calibration a comparison with the results of an independent method is advisable.

At higher thicknesses (≥ 5 nm) a comparison and calibration of ESCA data, measured with Al or Mg K α excitation, with ellipsometric thicknesses is possible and useful. At lower thicknesses the ellipsometric method becomes unreliable [3,6]. The exaggeration of thicknesses is mainly due to the inclusion of contamination layers and to a change in the optical parameters for very thin and/or disturbed layers.

Additionally, the error limit of the ESCA (Al, Mg) data increases rapidly

Table 1

Intensity ratios Si 2p(oxide)/Si 2p(element) for Zr M ζ and Al K α excitation and layer thicknesses d_{SiO}

Sample	Air exposure time (min)	Intensity ratio $I(\text{oxide})/I(\text{element})$		d_{SiO} (nm)	
		Zr	Al	Zr	Al
A	Before etching	11.55	0.571	0.97	0.86 ^{a)}
	5	0.28	0.09	0.12	(0.18)
	10	0.56	0.10	0.21	0.20
	55	0.93	0.12	0.30	0.23
	490	2.74	0.33	0.55	0.56
B	10	0.31	0.07	0.13	(0.15)
	15	0.53		0.20	
	79	1.19	0.19	0.35	0.35
	935	2.29	0.31	0.51	0.53

^{a)} $d_{\text{SiO}_2} = 1.14$ nm.

below $d \approx 0.5$ nm. The reason is the difficult separation of the small oxide intensity, related to the rather high escape depth of ≥ 2.5 nm (the Al-derived values for the smallest exposures are therefore given in parentheses in table 1). However, the use of an another radiation source, giving kinetic energies of the photoelectrons in the region of minimum escape depth (in our case Zr M ζ) and the comparison with NAA instead of ellipsometry allows us to extend the determination of the layer thicknesses to very low values, provided the layers are homogeneous and the interface between layer and substrate is not too rough. This is obviously the case for the layers investigated here, as can be seen from the good agreement between the Zr M ζ and the Al K α derived thicknesses in table 1. The same good agreement we found for several other samples (unpublished results), however, in some cases, e.g. after HF/HNO $_3$ etching of Si, we obtain remarkable differences between both thicknesses, pointing to a nonhomogeneous layer structure.

The oxide thicknesses, received with XPS (table 1) are shown together with the thicknesses, determined with NAA (standard deviation $\approx \pm 20\%$) from analogously treated samples, in fig. 2. The overall agreement is remarkably good. The correlation between the oxide layer thickness and the logarithm of the exposure time can be approximated by a straight line. Therefore we can conclude that the oxidation rate for HF etched Si<100> crystals in air at room temperature is logarithmic. The same was found by Raider et al. [3], for exposures of 1 h and higher, whereas our exposures start with 3 min. The growth rate is in our case ≈ 0.2 nm/decade; this agrees practically with the rate found by Raider et al. [3] (0.24 nm/decade, taken from fig. 3 of their

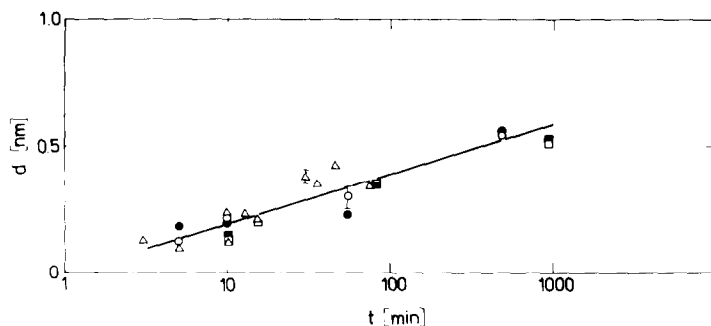


Fig. 2. Oxide thickness versus time of air exposure. ESCA: sample A, Al (●), Zr (○); sample B, Al (■), Zr (□); NAA (△).

paper). “Samples before etching” (table 1) are silicon wafers, which were stored in air at room temperature after polishing and after etching with HF at least for several months. Our thickness measurements of these samples by means of ESCA (1.14–1.27 nm) indicate that the estimated value of an equilibrium oxide thickness for oxide growth in air at room temperature (< 1.4 nm) given by Raider et al. [3] is accurate unless the doping concentration of the substrate is larger than $10^{19}/\text{cm}^3$ [3]. This value is considerably lower than that from previous indications which were based on ellipsometry [3].

5. Conclusions

(1) First we measured the oxide growth of etched $\langle 100 \rangle$ oriented silicon in air at room temperature for exposure times between 3 min and 1 h by means of ESCA and NAA.

(2) The results of the two independent methods for thickness measurements agree remarkably well.

(3) Our results of thickness measurements agree practically well with the values of Raider et al. [3] after higher exposure times to air (> 1 h): the growth rate is logarithmic and may be characterized by the value of 0.2 nm/decade.

(4) Our measurements indicate that the estimated value of an equilibrium oxide thickness in air for oxide growth at room temperature (< 1.4 nm) by Raider et al. [3] is accurate unless the doping concentration of the substrate is greater than $10^{19}/\text{cm}^3$ [3].

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